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(54) **EMULSIFIED HAIR CARE PREPARATION.**

(57) An emulsified hair care preparation comprising: (i) dimethylsilicone rubber represented by formula (I), wherein R^1 and R^2 each represents methyl or hydroxyl, and n is an integer of 4,000 to 9,000, (ii) dimethylsilicone oil, and (iii) polyhydric alcohol and nonionic surfactant.

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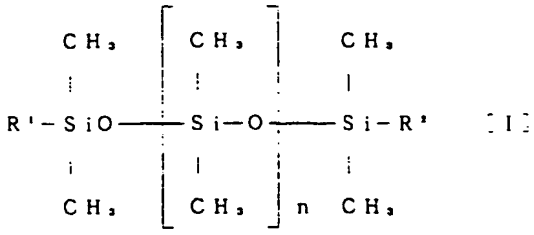


[I]

FIELD OF THE INVENTION

The present invention relates to an emulsified hair cosmetic providing excellent easy combing and a feeling of smoothness to hair and protecting hair against heat and brushing.

BACKGROUND OF THE INVENTION

Various hair cosmetics such as a hair treatment preparation, a hair rinse, etc. have been used to provide gloss and elasticity to hair, or to take care of injured hair. For example, in order to provide gloss to hair, a hair treating composition in which oily ingredients such as silicone oil, higher alcohol, liquid paraffin, ester oil, etc. are formulated have been used Further, in order to provide softness and antistatic effect to hair, a hair treating composition in which a cationic surfactant or a cationic polymer is formulated have been used. Furthermore, in order to protect hair against heat of drier, etc., a hair treating composition in which a water-soluble polymer is formulated have been used.

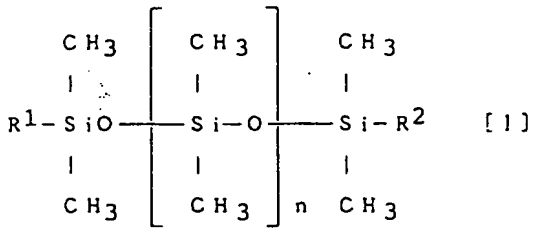
However, when a hair treating composition in which the above oily ingredients are formulated is applied to hair, it provides a feeling of extraneous matter such as sticking . The hair treating composition, itself also have sticking, therefore the physical resistance against combing or brushing becomes large. Further, a hair treating composition in which a cationic surfactant, a cationic high polymer is formulated electrically adsorbs only at the part of a surface of hair, charged negative, so that the adsorptivity is not enough and the homogeneity and the combing are not satisfactory. Furthermore, a hair treating composition itself in which a water-soluble polymer is formulated have a remarkable sticking and adhesion, therefore after treatment it provides a feeling of extraneous matter such as stiffness and the combing is not satisfactory.

In order to overcome these problems, a hair care product using a silicone rubber is recently provided (Japanese Patent Laid Open Application No. 313714/1988, Japanese Patent Laid Open Application No. 168609/1989). Further, there is a demand for a product having more excellent properties.

DISCLOSURE OF THE INVENTION

According to the present invention, there is provided an emulsified hair cosmetic which comprises

(i) a dimethylsilicone rubber of the formula:



[I]

wherein R^1 and R^2 are methyl or hydroxy; and n is an integer of 4000 to 9000;

(ii) a dimethylsilicone oil having the viscosity of 10 to 100000 centistokes at 25 °C;

(iii) one or more of polyhydric alcohol selected from the group consisting of propylene glycol, 1,3-butylene glycol and glycerin; and

(iv) one or more of nonionic surfactant selected from the group consisting of polyoxyethylene oleyl ether, polyoxyethylene cetyl ether, ethylene glycol stearate, diethylene glycol stearate, polyethylene glycol stearate, polyethylene glycol distearate and glyceryl stearate, the amount of (i) being 1/20 to 1/3 of the amount of (ii), the total amount of (iv) being not 7-fold more than the amount of (i) and being 1/2 to 2 of the amount of (iii).

The emulsified hair cosmetic of the present invention provides excellent easy combing and smooth feeling to hair and protects hair against heat and brushing.

Representative examples of dimethyl silicone rubber shown by the formula [I] which are used in the hair treating compositions of the present invention include Toshiba Silicone TSE-200 and TSE-200A manufactured by Toshiba Silicone Co., Ltd., Japan and the like, and one or more of them can be formulated in the emulsified hair cosmetic of the present invention in an amount of 0.01 to 10% by weight, preferably 0.5 to 2.0% by weight based on the total weight of the cosmetic. When the amount is less than 0.01% by weight, the effect for providing easy combing and a feeling of smoothness to hair becomes insufficient and, when

the amount is more than 10% by weight, viscosity of the dimethyl silicone rubber itself increases and it becomes difficult to emulsify.

A dimethyl silicone oil of (ii) is known as so-called nonvolatile dimethyl silicone oil having the viscosity of 10 to 100000 centistokes at 25 °C. When viscosity is less than 10 centistokes, the dimethyl silicone oil is easy to volatilize and durability of the effect of the hair cosmetic becomes inferior, and when viscosity is more than 100000 centistokes, the hair cosmetic becomes too viscous and a feeling of use becomes bad. Such the dimethyl silicone oil can be formulated in the emulsified hair cosmetic in an amount of 3 to 20-fold weight of silicone rubber (i). When the amount is 3-fold less than that of silicone rubber, viscosity of hair cosmetic increases and a feeling of use becomes bad. And when the amount is 20-fold more than the amount of silicone rubber, the properties of the hair cosmetic is adversely effected and the effect for providing easy combing becomes bad.

In the hair cosmetic of the present invention, the total amount of nonionic surfactant (iv) is not 7-fold more than the amount of silicone rubber (i), and is 1/2 to 2 of the amount of polyalcohol (iii). When the total amount of (iv) is 7-fold more than the amount of silicone rubber, the emulsification is stabilized but usability of the emulsion is adversely effected. Further, when the total amount of nonionic surfactant is out of the range of 1/2-fold to 2-fold amount of polyalcohol of (iii), the emulsion becomes unstable, and liable to separate with the passage of time.

A hair cosmetic of the present invention can be prepared in a form of milky lotion, blow agent, hair rinse, hair treatment or hair mousse by mixing desired ingredients and emulsifying them. Further, oily ingredients (such as cyclic silicone, triglyceride, ester oil, wax, etc.), coloring agents, perfumery, pH adjustors (such as phosphoric acid, citric acid, etc.), humectants (such as pyrrolidone carboxylate, lactic acid, etc.), solvents (such as water, ethanol, etc.), antistatic agents (such as cationic surfactant, etc.) can be formulated in the emulsified hair cosmetic of the present invention so far as they do not deteriorate the properties of the composition.

The following Examples and Comparative Examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof. All the %'s in Examples and Comparative Examples are by weight.

Example 1 to 6 and Comparative Examples 1 to 10

Each milky lotion like hair cosmetic was prepared by mixing the ingredients described in Table 1 and thereafter stirring according to a conventional method. The following items were evaluated by the use of these hair cosmetics. The results are also shown in Table 1.

Evaluation

Evaluation of a test sample was carried out according to the following method.

(1) Sticking and gloss immediately after application

These were evaluated by organoleptic test of practical use involving five professional panelists (female of the twenties).

0: Gloss, no sticking immediately after application
X: Sticking, no gloss immediately after application

(2) Resistance against combing after drying

A human hair (2g) treated with each test treating composition and dried was attached to a rheometer (Fudo Kogyo Co., Ltd., Japan). Maximum drag applied to the rheometer upon combing was measured and resistance against combing was calculated from the following formula:

$$\text{Resistance against combing (\%)} = \frac{\text{Resistance against combing after treatment}}{\text{Resistance against combing before treatment}} \times 100$$

(3) The number of hair cut

The number of hair cut after 7200 times of combing (a bundle of hair weighed about 2g: 119 non-treated hairs)

(4) Stability

After being allowed to stand at 40 °C for one month, separation (or creaming) was evaluated according to the following criteria.

0: Stable
X: Creaming or separation

(5) Overall evaluation

0: No sticking, easy combing and stable
X: Sticking, bad combing or unstable

Table 1

	Ingredients	Amount (% by weight) Examples 1	2	3	4	5	6	Comparative Examples 1	2	3	4	5	6	7	8	9	10
i	Dimethyl silicone rubber (R^1 and R^2=CH_3)	1.0	-	0.8	-	0.2	1.5	-	1.0	0.5	1.0	1.0	0.5	0.5	1.0	0.5	0.5
	Dimethyl silicone rubber (R^1 and R^2=OH)	-	1.0	-	0.5	-	-	-	-	-	-	-	-	-	-	-	-
ii	Dimethyl silicone oil (2cs)	-	-	-	-	-	-	-	-	-	5.0	-	-	-	-	-	-
	Dimethyl silicone oil (10cs)	-	5.0	-	-	2.0	10.0	-	-	-	-	-	-	-	-	-	-
	Dimethyl silicone oil (100cs)	5.0	-	-	5.0	2.0	-	5.0	2.5	12.0	-	-	5.0	5.0	5.0	5.0	5.0
	Dimethyl silicone oil (100000cs)	-	-	5.0	-	-	-	-	-	-	-	-	-	-	-	-	-
	Dimethyl silicone oil (1000000cs)	-	-	-	-	-	-	-	-	-	-	5.0	-	-	-	-	-
iii	Propylene glycol	1.0	-	-	1.0	0.5	-	1.0	-	-	1.0	-	-	5.0	1.0	1.0	1.0
	Glycerin	-	1.0	-	-	-	0.5	-	1.0	-	-	1.0	-	-	-	-	-
	1,3-Butylene glycol	-	-	1.0	-	0.5	0.5	-	-	1.0	-	-	-	-	-	-	-
iv	Polyoxyethylene oleyl ether (5EO)	1.2	-	-	0.5	-	0.5	1.2	1.2	1.2	1.2	1.2	1.2	1.2	-	2.0	1.5
	Polyoxyethylene cethyl ether (10EO)	-	0.3	-	0.2	-	0.8	-	-	-	-	-	-	-	-	2.0	1.0
	Glyceryl stearate	-	0.8	-	0.3	0.2	-	-	-	-	-	-	-	-	-	-	-
	Polyoxyethylene stearate (20EO)	-	-	1.2	-	1.0	-	-	-	-	-	-	-	-	-	-	-
	Ethanol	10.0	10.0	10.0	-	5.0	-	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10 0	10.0
	Isopropyl palmitate	1.0	-	-	0.5	-	-	1.0	-	-	-	-	-	-	-	-	-
	Tween 80	-	-	-	-	-	-	-	-	-	-	-	-	-	1.2	-	-
	Sodium lauryl sulphate	-	-	-	0.1	-	-	-	-	-	-	-	-	-	-	-	-
	Water	Remainder															

Example 7 (a blow-wave preparation)

Contd.

Result	Examples						Comparative Examples									
	1	2	3	4	5	6	1	2	3	4	5	6	7	8	9	10
Sticking immediately after application	0	0	0	0	0	0	0	X	X	0	X	-	-	-	X	X
Gloss of hair	0	0	0	0	0	0	0	X	0	X	0	-	-	-	X	X
Resistance against combing (%)	62.3	55.2	59.3	57.8	63.0	55.0	101.1	65.2	93.1	60.3	83.2	-	-	-	82.3	90.3
Resistance against combing (after drying by drier, %)	65.7	58.3	60.1	58.9	63.2	58.2	102.5	69.3	95.7	78.3	87.2	-	-	-	85.5	89.5
The number of hair cut	5	2	7	3	3	5	105	9	92	9	70	-	-	-	62	97
Stability	0	0	0	0	0	0	0	0	0	0	0	X	X	X	0	0
Overall evaluation	0	0	0	0	0	0	X	X	X	X	X	X	X	X	X	X

Ingredient A	Amount (%)
1) Propylene glycol	0.8
2) Polyoxyethylene oleyl ether (5 EO)	0.5
3) Polyoxyethylene stearate (2 EO)	0.2
4) Dimethyl silicone rubber (TSE 200A)	0.8
5) Polyoxyethylene lauryl ether sulfuric acid sodium salt	0.1
6) Dimethyl silicone oil (100 cs)	8.0

Ingredient B	Amount (%)
7) Water	remainder

Ingredient C	Amount (%)
8) 95% Ethanol	20 0

Ingredient D	Amount (%)
9) Perfume	0.1

To the ingredient A heated at 60 °C added the ingredient B heated at 60 °C and they were stirred to mix. Then, ingredients C and D were added while cooling. Alternatively, a mixture of surfactant and water-soluble polyalcohol may be prepared at first, and then an oily phase may be added.

Example 8 (a milky lotion type)

Ingredient A	Amount(%)
1) 1,3-Butylene glycol	1.8
2) Polyoxyethylene cetyl ether (5 EO)	1.2
3) Dimethyl silicone rubber (TSE 200)	1.0
4) Dimethyl silicone oil (20 cs)	19.0

Ingredient B	Amount (%)
5) Carbopol 941	0.3
6) Water	remainder

Ingredient C	Amount (%)
7) Triethanolamine	0.3
8) Water	2.7

Ingredient D	Amount (%)
9) Perfume	0.1

Ingredient B were mixed and kept at 80 °C. Separately, ingredient A were mixed and kept at 70 °C, and this was added to the above-described ingredient B, and these were stirred into uniformity. Thereafter, ingredient C and ingredient D were added to prepare a hair milky lotion.

Example 9 (a hair rinse

Ingredient A	Amount (%)
1) Stearyltrimethylammonium chloride	2.0
2) Dimethyl silicone rubber (TSE200A)	2.0
3) Dimethyl silicone oil (500 cs)	8.0
4) Self-emulsifiable glyceryl monostearate	1.0
5) Ethylene glycol monostearate	1.0

Ingredient B	Amount (%)
6) Glycerin	2.0
7) Preservative	trace
8) Coloring agent	trace
9) Water	remainder

Ingredient C	Amount (%)
10) Perfume	1.0

Ingredient B were mixed and kept at 75 °C, and to this added ingredient A which had been separately mixed and kept at 75 °C. To this added ingredient C while stirring and cooling to prepare a hair rinse.

Example 10 (a hair treatment type)

Ingredient A	Amount (%)
1) Dimethylbenzylammonium chloride	3.0
2) Dimethyl silicone rubber (TSE200)	1.5
3) Dimethyl silicone oil (10 cs)	10.0
4) Lanolin	1.0
5) Squalane	2.0
6) Self-emulsifiable glyceryl monostearate	3.0
7) Ethylene glycol monostearate	5.0
8) Cetyl alcohol	0.5

Ingredient B	Amount (%)
9) Propylene glycol	5.0
10) Sodium hyalronate	0.001
11) Preservative	trace
12) Water	remainder

Ingredient C	Amount (%)
13) Perfume	trace

Ingredient B were mixed and kept at 75 °C, and to this added ingredient A which had been separately mixed and kept at 75 °C. To this added ingredient C while stirring and cooling to prepare a hair treatment type composition.

Example 11 (a hair mousse)

Ingredient A	Amount (%)
1) Propylene glycol	1.0
2) Polyoxyethylene oleyl ether (5 EO)	1.0
3) Dimethyl silicone rubber (TSE200A)	0.3
4) Dimethyl silicone oil (100 cs)	4.0

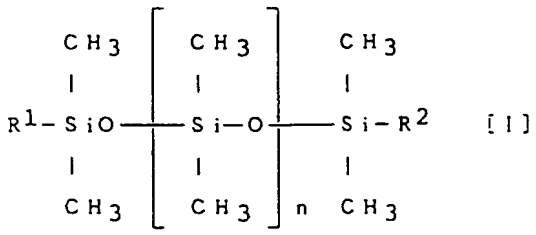
Ingredient B	Amount (%)
5) Witch-hazel extract	0.01
6) Polyvinyl pyrrolidone	0.8
7) Water	remainder

Ingredient C	Amount (%)
8) 95% Ethanol	10.0
9) Perfume	0.1

To the ingredient A heated at 60 °C added the ingredient B heated at 60 °C, and these were stirred to mix. Then, to this added the ingredient C while cooling to prepare an undiluted solution. 90 Parts of this undiluted solution and 10 parts of propellant were filled into an aerosol container to obtain a hair mousse.

Claims

1. An emulsified hair cosmetic which comprises
   (i) a dimethylsilicone rubber of the formula.



[I]

wherein R^1 and R^2 are methyl or hydroxyl; and n is an integer of 4000 to 9000;
(ii) a dimethylsilicone oil having the viscosity of 10 to 100000 centistokes at 25 °C;
(iii) one or more of polyhydric alcohol selected from the group consisting of propylene glycol, 1,3-butylene glycol and glycerin; and
(iv) one or more of nonionic surfactant selected from the group consisting of polyoxyethylene oleyl ether, polyoxyethylene cetyl ether, ethylene glycol stearate, diethylene glycol stearate, polyethylene glycol stearate, polyethylene glycol distearate and glyceryl stearate, the amount of (i) being 1/20 to 1/3 of the amount of (ii), the total amount of (iv) being not 7-fold more than the amount of (i) and being 1/2 to 2 of the amount of (iii).

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP91/00692

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl[5] A61K7/06

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	A61K7/06, A61K7/07, A61K7/075, A61K7/08, A61K7/09, A61K7/11, A61K7/13, A61K7/135, A61K7/135, A61K7/155

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

Jitsuyo Shinan Koho 1926 - 1991
Kokai Jitsuyo Shinan Koho 1971 - 1991

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	JP, A, 02-59510 (Hanasei Kagaku Kogyo K.K.), February 28, 1990 (28. 02. 90), (Family: none)	1
Y	JP, A, 02-59508 (L'Oreal), February 28, 1990 (28. 02. 90), & EP, A, 351297 & LU, A, 87273	1
Y	JP, A, 02-22212 (The Procter & Gamble Co.), January 25, 1990 (25. 01. 90), & EP, A, 333433 & AU, A, 8931409	1
Y	JP, A, 02-11506 (Lion Corp.), January 16, 1990 (16. 01. 90), (Family: none)	1
Y	JP, A, 01-168609 (Sunstar Inc.), July 4, 1989 (04. 07. 89), & EP, A, 323739 & AU, A, 8827588 & CN, A, 1034488 & US, A, 4943431	1

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
July 17, 1991 (17. 07. 91)	August 12, 1991 (12. 08. 91)
International Searching Authority	**Signature of Authorized Officer**
Japanese Patent Office	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	JP, A, 63-230620 (Coap Creen K.K.), September 27, 1988 (27. 09. 88), (Family: none)	1

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers . . , because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers . . , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim numbers . . . , because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.